

Improving the performance of eco-friendly co-extruded polyamide nanocomposite films

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The performance of polyamide/polyethylene multilayer nanocomposite films for food packaging was optimized by tuning the co-extrusion processing conditions and film layout.

There is great potential for nanotechnology to enhance the properties of food packaging (in terms of, e.g., the mechanical, barrier, and antimicrobial properties). There remain, however, a number of important issues to consider. These issues center on safety concerns, and the challenges around industrial scale-up. A feasible solution for overcoming one concern—the problem of possible nanoparticle migration—may be the use of a functional barrier between the nanomaterial and the food being packaged.

A wide range of studies have been devoted to polyamide (PA)-based nanocomposites.^{1–8} Such nanocomposites have found a wide range of applications in, for example, the automotive, packaging, and engineering industries. However, few investigations have been carried out on the use of multilayer systems for flexible film packaging applications.^{9–12}

We have developed multilayer packaging films that incorporate a PA/layered-silicate nanocomposite (as the oxygen barrier layer) and low-density polyethylene (PE, as the moisture-resistant and weldable layer).¹³ To fabricate our films, we used laboratory-scale blown co-extrusion equipment operating under different processing conditions and with varying film layouts. We subsequently tested their performance. Our aim is to determine the key parameters for performance improvement and to assess the potential applicability of these films on an industrial scale.

In particular, we fabricated the nanocomposite layers by melt-compounding copolyamide 6/66 (CS40LXW, Radici Group) with two different commercial organomodified layered silicates, i.e., Cloisite 30B (C30B) and Dellite 43B (D43B). Table 1 summarizes the characteristics of the coextruded structures (i.e., S1, S2, and S3) that we produced and subsequently analyzed in terms of their transport properties. We also performed overall migration tests to obtain preliminary

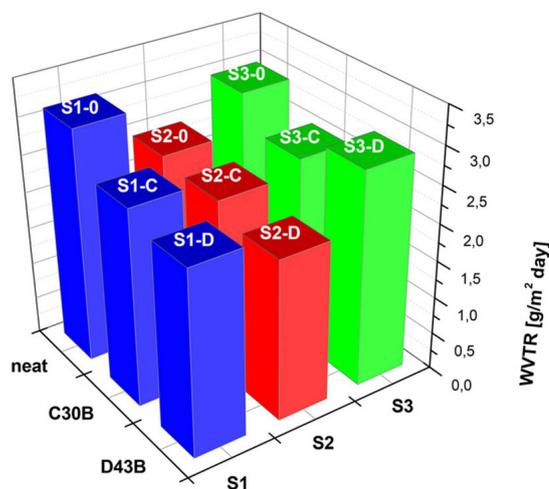


Figure 1. Water-vapor transmission rates (WVTR) of neat and nanocomposite copolyamide multilayer structures with different film layouts. The standard deviations of all WVTR values were less than 5%. C30B: Cloisite 30B. D43B: Dellite 43B. The structure types (S1, S2, and S3) are detailed in Table 1.

data regarding the possibility of using a functional barrier in flexible multilayer nanocomposite systems.

In Table 2, we compare the oxygen transmission rates (OTR) of the neat and nanocomposite multilayer structures for different film layouts. With respect to the corresponding unfilled systems, and compared to similar PA/PE commercial films,¹⁴ all the C30B and D43B-based nanocomposite multilayer films show a significant decrease in their OTR values (i.e., a significant increase in their oxygen barrier properties) of 50–60%. Moreover, while the OTR values of the unfilled systems increase with a decreasing oxygen-barrier (PA) layer thickness and with increasing film-stretching conditions (i.e., from structure types S1 to S3), we observed different trends for the hybrid multilayer

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Table 1. Nomenclature and description of the multilayer films produced with different layouts. tie: The adhesive layer (i.e., a linear low-density polyethylene, PE, grafted by maleic anhydride). PA: Polyamide.

Film type	Film nomenclature and layout	Layer thicknesses [μm]	Total film thickness [μm]	Draw ratio
	S1-0: PA/tie/PE			
S1	S1-C: PA+C30B/tie/PE	45/8/27	80 ± 1	5
	S1-D: PA+D43B/tie/PE			
	S2-0: PA/tie/PE			
S2	S2-C: PA+C30B/tie/PE	35/8/27	70 ± 3	6.5
	S2-D: PA+D43B/tie/PE			
	S3-0: PA/tie/PE			
S3	S3-C: PA+C30B/tie/PE	35/8/17	60 ± 2	8
	S3-D: PA+D43B/tie/PE			

films. In particular, the OTR values of the nanocomposite films remain essentially unchanged from type S1 to type S2. In fact, as our x-ray diffraction and differential scanning calorimetry results show,¹³ the nanoclay in the S2 system achieved a higher intercalation level with respect to the S1 system. This suggests that there are a higher number of immobilized PA chains in the thinner S2 film. Moreover, we observe an increase in the OTR values for the hybrid films with S3 structures (compared with S2). We propose that the re-aggregation of clay platelets is responsible for an enhancement in the mobility of PA chains and the resultant increase in the OTR values of the films.

We also analyzed the barrier performance of the multilayer films in terms of their water-vapor transmission rates (WVTR), and evaluated the effect of reducing both the PA and the PE layer thickness on WVTR values. Comparisons between these films are shown in Figure 1. Since the water-vapor barrier function is essentially carried out by the PE layer, the WVTR values were on average higher for the systems with a thicker PA layer (i.e., S1-0, S1-C, and S1-D) due to its hydrophilic nature. However, it is notable that the presence of both nanofillers slightly reduced the WVTR results of the hybrid films compared to the corresponding unfilled structures. This barrier improvement was more significant (20%) in the samples characterized by a thicker PA layer (S1-C and S1-D). As expected, the reduction of the PE layer (from type S2 to type S3 structures) determined an increase of the WVTR values in all the systems.

We then performed overall migration measurements on the samples to preliminarily verify the compliance of our multilayer films with the EU regulations for food-contact materials (i.e., Regulation EU 10/2011). The results of these tests, carried out on the coextruded structures, are reported in Table 3. We found that our multilayer films obtained values significantly lower than the legislation limit of

Table 2. Oxygen transmission rates (OTR) of neat and nanocomposite copolyamide multilayer structures with different film layouts. The standard deviations of all OTR values were less than 10%.

Relative thicknesses PA/tie/PE					
[45/8/27] [μm]		[35/8/27] [μm]		[35/8/17] [μm]	
Film	OTR [$\text{cm}^3/\text{m}^2\text{d}$]	Film	OTR [$\text{cm}^3/\text{m}^2\text{d}$]	Film	OTR [$\text{cm}^3/\text{m}^2\text{d}$]
S1-0	31.2	S2-0	39.2	S3-0	41.8
S1-C	16.7	S2-C	17.0	S3-C	23.1
S1-D	15.9	S2-D	20.1	S3-D	24.0

Table 3. Overall migration data for selected multilayer films after contact with rectified olive oil (simulant D2) at 40°C for 10 days, using migration cells for one-side contact.

		Overall migration [mg/dm^2]		
		Neat	C30B	D43B
Film type	Clay type			
S1		0.21 ± 0.16	1.54 ± 1.30	–
S2		0.33 ± 0.22	0.25 ± 0.19	0.28 ± 0.20
S3		0.19 ± 0.14	0.28 ± 0.25	–

10mg/dm².

In summary, we have developed PA/PE multilayer films with nanoclays incorporated into the PA layer that are suitable for use in food packaging. We found that the systems with thinner nanocomposite layers and, in particular, the nanocomposite filled with C30B show the most significant increase (about 60%) in the oxygen barrier properties. This is because the presence of two hydroxyl groups in the C30B structure promotes affinity with the carbon-oxygen bonds in the PA backbone by increasing polar interactions between the phases. The improvements to water-vapor-permeation resistance were less significant, however (achieving a maximum of approximately 20%) due to the intrinsic hydrophilic nature of PA. The lowest WVTR values were measured for the thickest nanocomposite film systems that incorporated D43B filler in the PA layer. This organomodifier has a higher degree of hydrophobicity with respect to C30B. Bearing in mind the safety issues of these hybrid films, the possibility of food contamination by the nanoparticles' anionic intercalating agent appears to be the most important issue. In our future work we will therefore conduct more accurate specific migration tests. We will also perform shelf-life measurements on selected foods packaged inside of our nanocomposite multilayer films.

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